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Selective removal of Hg(II) with polyacrylonitrile-2-amino-1,3,4-thiadiazole chelating resin: Batch and column study

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HIGHLIGHTS

- A novel chelating resin of PAN-ATD was synthesized via one-step reaction.
- PAN-ATD exhibited good overall adsorption properties and could be easily eluted to Hg(II).
- High adsorption capacity and selectivity are attributed to the nitrogen groups.
- PAN-ATD can be potentially used in waste treatment and detection area.

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ABSTRACT

A novel chelating resin, polyacrylonitrile-2-amino-1,3,4-thiadiazole (PAN-ATD), was prepared via one-step reaction and its structure was characterized by elemental analysis and FT-IR. The adsorption properties of the resin for Hg(II) were investigated by batch and column experiments. Batch adsorption results showed that PAN-ATD had high affinity towards Hg(II) and the maximum adsorption capacity estimated from the Langmuir model was 526.9 mg/g at 308 K. The adsorption kinetic and equilibrium data were well fitted to the pseudo-second-order model and the Langmuir isotherm model, respectively. Furthermore, the resin can be easily regenerated and reused with less than 10% loss of adsorption capacity. Also, the resin and its metal complexes were studied by SEM, TGA, and energy dispersive X-ray spectroscopy (EDS). With good overall properties (a high selectivity adsorption capacity, easy to be regenerated and stable application capacity) PAN-ATD resin can not only be used in selective removal of Hg(II) from waste solution, but also be used for preparation of the separation and enrichment column applied in the analysis and detection area.

1. Introduction

Heavy metal contamination is becoming one of the main concerns of environmentalists due to their non-biodegradability and high toxicity even at trace concentrations [1]. Mercury, as one of the important heavy metals, is released to the environment from wastewater such as paper, oil refinery, pulp, chlor-alkali manufacturing, pharmaceutical, and battery manufacturing industries [2]. Exposure to mercury can damage the nervous system in humans, especially for the developing nervous system of young children [3]. Hence, removing heavy metals from wastewater to reduce its hazards is a critical task in the perspective of environment and health.

Various technologies have been applied in removing mercury from industrial effluents, among which some are expensive, inefficient or polluting, such as solvent extraction, reduction, coagulation, reverse osmosis, chemical precipitation, membrane separation, and ion exchange [4,5]. In contrast, adsorption is regarded as a guaranteed and practical treatment method by utilizing its low cost, high adsorption capacity, easy metal recovery and good reusability. And a wide range of materials can be used to remove mercury from solutions such as chitosan [5], activated carbon [6],

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carbon nanotubes [7,8], Pumice-supported nanoscale [9], guar gum [10], silica nanocomposite [11,12], aluminosilicates [13], polythioamides [14,15], MCM-41 [16], zinc oxide nanoparticles [17], barley husk silica [18], magnetite (Fe_3O_4) particles [19], and polyacrylonitrile [20–22]. Polyacrylonitrile (PAN) is an ideal polymeric matrix with a series of merits such as solvent resistance, thermal and mechanical stability, abrasion resistance, and high tensile strength [22]. Active nitrile groups (C≡N) in PAN can easily be converted into a number of new functional groups via special reactions. Deng et al. [20,21] used the aminated polyacrylonitrile fibers to remove copper, lead, and chromium ions from aqueous solutions, but the metal adsorption capacity was not very ideal. Our initial report suggested that the 2-aminothiazole functionalized polyacrylonitrile resin containing nitrogen and sulfur atoms can be used for selective adsorption of Hg(II) from solutions with a good adsorption capacity [22].

In this work, as a continuation of our initial work, we design another novel chelating resin (PAN-ATD) by grafting 2-amino-1,3,4-thiadiazole (ATD for short) on the surface of polyacrylonitrile beads. The synthetic resin was characterized by FT-IR, elemental analysis, TGA and DSC. The adsorption capability for Hg(II) in the aqueous solution had been investigated by a series of batch and column experiments. To further understand the adsorption process, the adsorption kinetics, isotherms and the thermodynamic properties of the adsorption of Hg(II) on the synthetic resin were also clarified. The recovery of Hg(II) and reusability of the adsorbents were also studied in detail.

2. Materials and methods

2.1. Materials and chemicals

Mesoporous-type cross-linked polyacrylonitrile beads (PAN), cross-linked with 7% divinylbenzene (DVB), nitrogen content 22.18%, functional groups content 15.83 CN mmol/g, specific surface area 27.8 m^2/g, pore size 25.1 nm, were purchased from Chen Guang Chemical Industrial Institute of China. Aqueous solutions of ions at various concentrations were prepared from $NiSO_4{\cdot}6H_2O$, $HgCl_2$, $CuCl_2{\cdot}2H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $Cd(NO_3)_2{\cdot}4H_2O$, and $Pb(NO_3)_2$ and were used as sources for Ni(II), Hg(II), Cu(II), Zn(II), Cd(II), and Pb(II), respectively. All other reagents and solvents were of analytical grade and used as received without further purification.

2.2. Measurements

FT-IR spectra were scanned in the region of 400–4000 cm^{-1} in KBr pellets on NICOLET 380 FT-IR spectrophotometer. C, N, and S elements were analyzed by a Vario EL III Elemental Analyzer. The specific surface area and the mean pore size of the resins were determined on an Autosorb-1 automatic surface area and pore size analyzer. Thermogravimetric analysis in a range of temperature 50–1000 °C by 20 °C min^{-1} under the protection of nitrogen on a TGA instrument; Differential scanning calorimeter (DSC) was recorded on a HCR-1 DSC under N^2 atmosphere (20 cm^3 min^{-1}) at 20 °C min^{-1}. The shapes and surface morphology of the resins were observed by means of a HITACHI S-3000N scanning electron microscope (SEM), in conjunction with SEM imaging. The elemental compositions of the resins were analyzed by energy-dispersive spectrometer (EDS). The concentrations of Hg(II) and the coexistent metal ions were determined by Perkin Elemer Optima 2100DV inductively coupled plasma optical emission spectrometer (ICP-OES). The respective zeta potentials of PAN-ATD resins were determined by a zeta potential analyzer (Malvern Zetasizer Nano ZS90). The sample was shaken in the DSHZ-300A temperature constant shaking machine. Mettler Toledo delta 320 pH meter was used for pH measurement.

2.3. Preparation of PAN–ATD

The preparation procedure is simple and described as follows: 0.5 g of PAN beads and 300 mL of *N*,*N*-dimethylformamide (DMF) were added into a 500 mL three-neck round-bottom flask, swelling over night. Then, 3.20 g of ATD (molar ratio of reagent (ATD/PAN) = 4) and a small amount of metallic sodium used as catalyst were added to the flask. The mixture reacted for 14 h at 140 °C with 100 rpm stirring speed under a nitrogen atmosphere. The solid product was carefully washed thoroughly with DMF and deionized and then with acetone and ether. After that the obtained resin was dried in vacuum at 50 °C. The conversion of the functional group of the synthetic resin can be calculated from sulfur content by the following equations:

$$F_c = \frac{S_c}{32.07 \times n_s} \times 1000 \quad (1)$$

$$x = \frac{F_c \times 1000}{F_0 \times 1000 - F_c \times M_L \times F_0} \quad (2)$$

where F_0 (15.83 mmol of CN/g) and F_c are the contents of the functional group of polyacrylonitrile and the resin synthesized, respectively, x is the functional group conversion (%), M_L is molar mass of the ligands (mol/g), n_s is the number of sulfur atoms of ligand molecules, and S_c is the sulfur content of the synthetic resin (%).

2.4. Batch adsorption experiments

Batch experiments were carried out to investigate the Hg(II) adsorption property on the prepared PAN-ATD resin by placing 15.0 mg resin in a series of flasks containing 30 mL of the studied metal ions at the desired initial concentration and pH. Then the contents of the flasks were shaken in a flask-shaker at specific temperature for a given time with a speed of 100 rpm. The residual concentration of the studied metal ions in the solution was determined by ICP. The adsorption capacity (Q, mg/g) and distribution coefficient (D, mL/g) were calculated with the following expression:

$$Q = \frac{C_0 - C_e}{W} V \quad (3)$$

$$D = \frac{C_0 - C_e}{W C_e} V \quad (4)$$

where C_0 is the initial concentration of Hg(II) (mg/mL), C_e is the residual concentration of Hg(II) in solution (mg/mL), V is the solution volume (mL), and W is the resin dry weight (g). The above batch adsorption experiments for the adsorption of Hg(II) by PAN-ATD in aqueous solutions were performed at different pH values, contact times, initial concentrations of Hg(II) and temperatures. The operating variables studied for the extent of adsorption were pH, contact time, initial concentration and temperature.

2.5. Column adsorption experiments

Column experiments were carried out in a fixed-bed mini glass column (Φ3 mm × 30 cm) under the optimum pH 6.5 obtained from the batch experiments at a constant temperature of 298 K, which is close to the environmentally relevant conditions. Then, 100.0 mg PAN-ATD was presoaked in the column for 24 h before the experiment began. In order to avoid the channeling of the effluent, a certain concentration of Hg(II) solution in a constant flow rate was passed continuously through the stationary bed of sorbent in up-flow mode. The outgoing Hg(II) concentration was determined at different time intervals as described above.